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Combined clumped isotope measurements resolve kinetic biases in carbonate formation temperatures

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Reaction kinetics involved in the precipitation of carbonates can introduce large scatter and inaccuracies in the temperatures derived from their $\delta^{18}\text{O}$ and Δ_{47} values. Advances in mass spectrometry instrumentation recently enabled high-precision analysis of the ^{18}O - ^{18}O clumping in carbonate minerals (Δ_{48}), despite the relatively low natural abundance of $^{12}\text{C}^{18}\text{O}^{18}\text{O}$, the main isotopologue contributing to the Δ_{48} signal (1). Measurements of Δ_{48} , when combined with Δ_{47} , can yield additional insights into kinetic effects and the carbonate formation environment (2).

Here we report high-precision Δ_{47} and Δ_{48} values of speleothem carbonates, modern coral skeletons, a brachiopod, and a belemnite. We constrained equilibrium in Δ_{47} vs Δ_{48} space by anchoring empirically derived Δ_{47} vs temperature and Δ_{48} vs temperature relationships to a Devils Hole mammillary calcite, known to be precipitated at extremely slow rates at a constant $33.7(\pm 0.8)$ °C and water oxygen isotope composition. Our results, compared to theoretical predictions, provide the most substantial evidence to date that the isotopic disequilibrium commonly observed in speleothems and scleractinian coral skeletons is inherited from the dissolved inorganic carbon pool of their parent solutions. Data from an ancient belemnite imply it precipitated near isotopic equilibrium and confirm the warmer-than-present temperatures at Early Cretaceous southern high latitudes. The presence of similar kinetic departure in a brachiopod but not in a belemnite suggests that the current discrepancy between belemnite and brachiopod-based temperature estimates in the geologic record is most likely related to a greater kinetic bias in the isotopic composition of brachiopod shells.

We demonstrate that the combined clumped isotope method makes it possible to identify carbonates that did not precipitate in thermodynamic equilibrium from their parent water. Our results highlight the potential that the combined clumped isotope analyses hold for accurate

paleoclimate reconstructions and the identification of the kinetic fractionation processes dominant in carbonate (bio)mineralisation.

(1) Fiebig et al. (2019), <https://doi.org/10.1016/j.chemgeo.2019.05.019>

(2) Guo, W. (2020), <https://doi.org/10.1016/j.gca.2019.07.055>